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（ 続紙 1 ）

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| 論文題目 | Effect of Surfactants on the Behaviors and Transport of Metal Oxide Nanomaterials in Aqueous Matrices and Porous Media（金属酸化物ナノ材料の水溶液マトリックスと多孔質体中での挙動と輸送における界面活性剤の影響） | | |

（論文内容の要旨）

This thesis presents the study proving an insight of the effect of surfactants on the aggregation, sedimentation, and transport of $TiO_2$ and ZnO engineered nanomaterials (ENMs) as a function of different water matrices, which are contributive to the environmental risk assessment of the engineered nanomaterials.

**Chapter 1** Introduction describes the background that motivates this research to be carried out, the objectives, the study area and the systematics of this research.

**Chapter 2** Review of literatures concerning the application, fate/transport, and environmental risks of $TiO_2$ and ZnO ENMs.

**Chapter 3** The adsorption of surfactants and the resulted effect on the behaviors of $TiO_2$ and ZnO ENMs were studied after a 24-h batch reactor experiment, and then the sedimentation of the aggregates of $TiO_2$ and ZnO ENMs were observed with a UV-spectrophotometer at a wavelength of 378 nm. It was found that both SDS and NP-9 surfactant can be apparently adsorbed by $TiO_2$ and ZnO ENMs, and Langmuir model can be well applied to the fitting of the adsorption isotherms. Next, the presence of both surfactants effectively reduced the aggregation of two ENMs when surfactant concentration exceeded 0.015% as observed by both dynamic scattering lightening (DSL) and scanning electronic microscopy (SEM). The SDS surfactant remarkably affected the zeta potential of $TiO_2$ and ZnO nanomaterials, and the absolute value of nanomaterials’ zeta potential decreased at first and then significantly increased with growth of SDS concentration. This process remarkably increased the electrical repulsive forces between nanoparticles, and hence reduced the aggregation and increased the stabilities of the aggregates of both $TiO_2$ and ZnO nanomaterials. As for the non-ionic NP-9 surfactant, the surfactant covered the surface of nanomaterials, hence reduced the aggregation and increased the stability of both nanomaterials. In a 24-h sedimentation observation, it was found the presence of both surfactants significantly retarded the sedimentation of $TiO_2$ and ZnO aggregate, and the increase of concentration of surfactants resulted stronger retardation on the sedimentation of the aggregate of ENMs.

**Chapter 4** The effect of surfactants on the behaviors of $TiO_2$ and ZnO ENMs in environmental conditions and six realistic water samples were explored. It was found that as pH increase from 6.0 to 9.0, the aggregate size of $TiO_2$ and ZnO ENMs varied significantly after 24-h batch reactor experiment. In addition, as the ionic strength increased to 50 mM, the aggregation of ENMs increased significantly. However, the introduction of surfactants reduced the aggregate size of both $TiO_2$ and ZnO ENMs as the function of pH and ionic strength. In six natural water matrices, the aggregation of both $TiO_2$ and ZnO ENMs were found most significant in Yangtze river water, and the ionic strength were thought to be a major reason for the increased aggregation of ENMs. With the presence of surfactant, however, both aggregation and sedimentation of ENMs were found to be retarded, and the ionic SDS was found more effective than nonionic NP-9 surfactant.

**Chapter 5** The effect of surfactants on the transport of $TiO_2$ and ZnO ENMs in saturated porous media was investigated as a function of anionic and nonionic surfactant concentration, pH of solutions, flow velocity and natural water samples. It was found surfactants enhanced the transport of $TiO_2$ and ZnO ENMs saturated porous media while a pH approaching the point of zero charge of $TiO_2$ and ZnO ENMs limited their transport. The deposition process, a retention mechanism of $TiO_2$ and ZnO ENMs saturated porous media was impacted by surfactant and pH. The electrostatic and steric repulsion forces in connection with the size of $TiO_2$ and ZnO aggregates and flow velocity impacted the single-collector efficiency and attachment efficiency which dictated the maximum transport distance of $TiO_2$ and ZnO ENMs. The increase of flow velocity allowed $TiO_2$ and ZnO ENMs to increase the maximum transport distances. And the presence of both SDS and NP-9 further increased the transport distances of $TiO_2$ and ZnO ENMs in porous sand media.

**Chapter 6** All the important findings of this study are summarized and emphasized.

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（論文審査の結果の要旨）

本論文は、工業用ナノ材料(ENMs)の水溶液および多孔質媒体中における挙動と輸送に対する水質と界面活性剤の影響を実験的に検討したものである。得られた主な成果は以下のとおりである。

１） 界面活性剤である陰イオン性ドデシル硫酸ナトリウム（SDS）と非イオン性ノニルフェノールエトキシレイト（NP-9）の、典型的 ENMs である $TiO_2$ と ZnO への水溶液中におけるバッチ吸着試験を行い、SDS と NP-9 は $TiO_2$ および ZnO の ENMs に吸着すること、その吸着等温線は Langmuir モデルに従うことを示した。また、SDS は用いた ENMs のゼータ電位への影響が強く、SDS 濃度の増加に従い、最初は ENMs のゼータ電位は減少するが、さらに SDS 濃度を増加させると ENMs のゼータ電位は大きく増加すること、界面活性剤濃度が 0.015%を超えると、2 つの ENMs の凝集が明らかに遅れることを示した。

２） 6 種類の環境水を用いたバッチ試験において、pH の 6.0 から 9.0 の変化で $TiO_2$ と ZnO の ENMs のフロックサイズは大きく変化した。また、イオン強度を 50mM に増加させても、フロックサイズは増大した。本研究で用いた環境水では、$TiO_2$ と ZnO の ENMs のフロックサイズは共に揚子江河川水が最大であり、その主たる理由はイオン強度の違いであると考えられた。また、環境水においても界面活性剤の存在で凝集は遅れること、その効果はイオン性の SDS の方が非イオン性の NP-9 よりも大きいことを示した。

３） 多孔質媒体としての砂カラム中の飽和流において、$TiO_2$ と ZnO の ENMs のカラム中移動距離と界面活性剤濃度、流速、pH との関係を調べ、ENMs のカラム中移動距離は流速の増加と SDS や NP-9 の存在によって増加すること、pH が電荷零点に近づくと移動は抑制されることなどを示した。

以上の結果は、近年、使用量が増加している ENMs の、環境水中における凝集、輸送、堆積に及ぼす水質などの影響を明らかにするものであり、ENMs の環境リスク評価確立に大きく貢献するものであって 、学術上、実際上寄与するところが少なくない。よって、本論文は博士（工学）の学位論文として価値あるものと認める。また、平成 29 年 2 月 22 日、論文内容とそれに関連した事項について試問を行って、申請者が博士後期課程学位取得基準を満たしていることを確認し、合格と認めた。